



## **Corrigendum to "Microbial pesticide removal in rapid sand filters for drinking water treatment - Potential and kinetics" [Water Res. 48 (2014) 71-81]**

**Hedegaard, Mathilde Jørgensen; Albrechtsen, Hans-Jørgen**

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# Corrigendum to "Microbial pesticide removal in rapid sand filters for drinking water treatment – Potential and kinetics" [Water Res. 48 (2014) 71-81]

*Mathilde J. Hedegaard<sup>1,\*</sup>, Hans-Jørgen Albrechtsen<sup>1</sup>*

<sup>1</sup>DTU Environment, Technical University of Denmark (DTU), Miljøvej, Building 113, DK-2800 Kgs. Lyngby, Denmark

\*Corresponding author: telephone (+45) 4525 1478, Email: [mjhe@env.dtu.dk](mailto:mjhe@env.dtu.dk)

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The authors regret to inform the readers that two stock solutions of [ $^{14}\text{C}$ -carbonyl-]bentazone and [ $^{14}\text{C}$ -ring-]dichlorprop has been mixed-up.

Recent experiments gave results which were in conflict with results from our previous experiments on degradation of bentazone, reported in Hedegaard and Albrechtsen (2014) and this lead us to realize the mix-up of the two  $^{14}\text{C}$ -pesticide stock solutions. Thus, references in Hedegaard and Albrechtsen (2014) to a result on [carbonyl- $^{14}\text{C}$ ]bentazone or just bentazone was actually a result on [Ring-U- $^{14}\text{C}$ ]dichlorprop and the results in this paper has to be corrected accordingly. However, the overall conclusion, that a substantial microbial pesticide removal is possible within the contact time of rapid sand filters, remains valid.

The aim of this corrigendum is to present the corrected results. Hence, tables and figures presented in this corrigendum are corrected and should replace the erroneous versions in the original paper. Furthermore, results from a series of experiments conducted with a new batch of [Carbonyl- $^{14}\text{C}$ ]bentazone is included to present degradation of bentazone in filter sand.

We have quality checked the  $^{14}\text{C}$ -stock-solutions of all the applied pesticides (Mecoprop, Glyphosate, Benzene-ring-U- $^{14}\text{C}$ -Bentazone and p-Nitrophenol), and verified that they all complied with the paper.

The removal potential of pesticides in rapid sand filters is thereby extended to include five pesticides: Mecoprop, Glyphosate, Bentazone, p-Nitrophenol and Dichlorprop.

The headings used in this corrigendum refer to the headings in the original paper (Hedegaard and Albrechtsen, 2014).

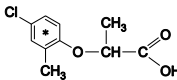
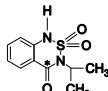
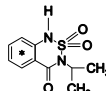
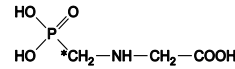
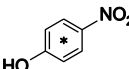
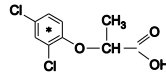
## Materials and methods

### Chemicals

Instead of the stated [ $^{14}\text{C}$ -carbonyl-]bentazone, [Ring-U- $^{14}\text{C}$ ]dichlorprop was investigated in the experiments (Table 2). To investigate bentazone removal we conducted a new series of investigations with a new batch of [Carbonyl- $^{14}\text{C}$ ]bentazone (Izotop, Institute of Isotopes Co., Ltd., Hungary) (Table 2).

The chemical identity of the  $^{14}\text{C}$ -stock-solutions of all the investigated pesticides were verified: Mecoprop (GC-MS), Glyphosate (HPLC-DAD), Benzene-ring-U- $^{14}\text{C}$ -Bentazone (HPLC-DAD),

**Table 2.** Information on investigated pesticides and metabolites

	Mecoprop	Bentazone		Glyphosate	p-Nitrophenol	Dichlorprop
Type and use of pesticide	The phenoxy acid is a herbicide used in agriculture, horticulture and for domestic purposes. Partially banned in Denmark in 1997. (The Danish Ministry of the Environment, 2011; Buss et al., 2006)	Herbicide used in cultivated areas, which is legally used in the European-Union. (EU pesticide database, 2013; Boivin et al., 2004)		The trade name is Roundup and it is the most sold herbicide for weed control in agriculture, silviculture, urban areas worldwide. (Woodburn, 2000; Borggaard and Gimsing, 2008)	Metabolite of the insecticide parathion, which is banned in the Europe Union (GEUS, 2011; Schilmann et al., 2009; The Council of the European Communities, 1991; The Commission of the European Communities, 2001)	The phenoxy acid is a herbicide used in agriculture and was partially banned in Denmark in 1997. (Tomlin, 2003; The Danish Ministry of the Environment, 2011)
Detection in active Danish drinking water wells 1992-2010 (GEUS, 2011)	2.5%	2.7%		1.7%	3.2%	2.0%
≥0.1µg/L (GEUS, 2011)	0.1%	0.4%		0.0%	0.0%	0.2%
Sorption in aquifer sediment	Mobile (Agertved et al., 1992; Tuxen et al. 2000)	Mobile (Clausen et al., 2001; Boivin et al., 2004)		Low mobility (Vereecken, 2005)	Mobile (Nielsen et al., 1996)	Mobile (Tuxen et al., 2000)
Volatility, K <sub>H</sub> (M/atm)	Non-volatile 4.65E+05 (EU Pesticide Database, 2013)	Non-volatile 1.41E+06 (EU Pesticide Database, 2013)		Non-volatile 4.83E+08 (EU Pesticide Database, 2013)	Non-volatile 7.79E+04 (Trempe et al., 1993)	Non-volatile 1.5E+07 (Tomlin, 2003)
)Degradability	Degraded weakly under anaerobic conditions (Janniche, 2010)	Difficult to degrade in aquifers (Albrechtsen et al., 2001; Broholm et al., 2001)		Degradable under aerobic and anaerobic conditions (Borggaard and Gimsing, 2008; Rueppel et al., 1977)	Degraded in aerobic aquifers (Nielsen et al., 1996)	Degradable (Tomlin, 2003)
<b>Radiochemicals</b>						
Position of <sup>14</sup> C-label	Ring- <sup>14</sup> C	Carbonyl- <sup>14</sup> C	Benzene-ring-U- <sup>14</sup> C	Phosphonomethyl- <sup>14</sup> C	<sup>14</sup> C(U)	Ring-U- <sup>14</sup> C
						
Radio-chemical purity (%)	> 95	100	99	99	> 99	99
Specific activity (mCi/mM)	23	40	20	50	77	25
Solvent of stock solution	Acetonitrile	Methanol	Methanol	Sterile water	Ethanol	Methanol
Producer	Izotop, Institute of Isotopes Co., Ltd., Hungary	Izotop, Institute of Isotopes Co., Ltd., Hungary		ARC American Radiolabeled Chemicals, Inc., USA	ARC American Radiolabeled Chemicals, Inc., USA	Izotop, Institute of Isotopes Co., Ltd., Hungary., Hungary

[Carbonyl-<sup>14</sup>C]bentazone (HPLC-DAD) and p-Nitrophenol (GC-MS). Experimental conditions including initial concentrations of dichlorprop and bentazone appear in Table 3.

### Experimental procedure ‘Removal kinetics – Bentazone’

The conditions in the experiment were identical with the conditions in ‘Removal kinetics’ (Table 3), except that the experiment only lasted for one hour, to mimic the removal within the contact time of the filters. Oxygen concentrations in the microcosms were monitored by oxy-spots throughout the experiment to ensure aerobic conditions.

### Experimental procedure ‘Removal potential – Bentazone’

The conditions in the experiment were identical with the conditions in the experiment ‘Effect of oxygen’ to ensure a surplus of oxygen throughout the entire experimental period of seven days (Table 3).

**Table 3.** Initial conditions in the microcosms in the different experiments. Added amount of filter sand and water appear as well as the initial concentration of the added pesticides. Investigated waterworks were; Islevbro (I), Sjølsø Plant I (SPI) and Sjølsø Plant II (SPII).

	Potential of filter sand			Removal kinetics - Dichlorprop	Effect of oxygen	Removal kinetics - Bentazone	Removal potential - Bentazone
Waterworks	I	SPI	SPII	SPII	SPII	SPII	SPII
Filter sand (g)	250	250	250	250	100	250	100
Water (mL)	100	100	100	100	100	100	100
Initial concentration							
Mecoprop (µg/L)	0.38	0.04	0.03	-	-	-	-
Glyphosate (µg/L)	-	0.05	0.05	-	-	-	-
p-Nitrophenol (µg/L)	-	0.16	0.16	-	-	-	-
[Ring-U- <sup>14</sup> C]Dichlorprop (µg/L)	0.2	0.2	0.2	0.2/0.9/4.2	0.6	-	-
[Benzene-ring-U- <sup>14</sup> C]Bentazone (µg/L)	-	-	-	0.16	-	-	-
[Carbonyl- <sup>14</sup> C]Bentazone (µg/L)	-	-	-	-	-	0.06	1.0

- no data

## Results and discussion

### Degradation potential of filter sand

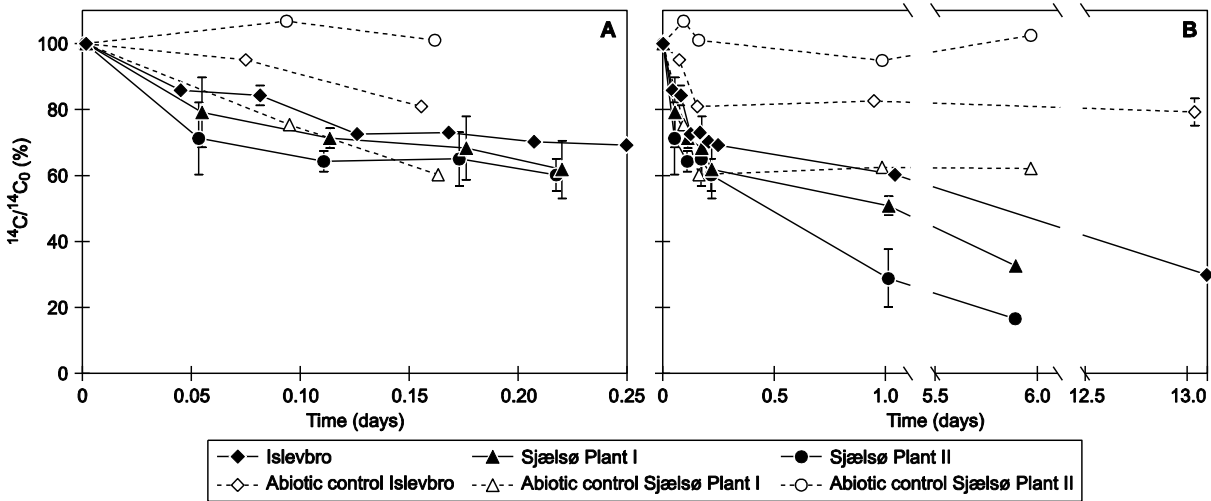
A substantial removal potential of the pesticides MCPP, dichlorprop, glyphosate and the degradation product 4-nitrophenol was detected in filter sand from three Danish waterworks (Table 4). The largest biological removal of dichlorprop was detected at Sjælsø Plant II (Figure 1), where also dichlorprop, glyphosate and 4-nitrophenol were mineralized (Table 4).

**Table 4.** Fractionation of  $^{14}\text{C}$ -pesticide after incubation with filter material from different filter sands. The fraction of  $^{14}\text{C}$  (or  $^{14}\text{CO}_2$ ) of the initial amount of  $^{14}\text{C}_0$  is shown at two selected times. Data are from microcosms (two replicates) and abiotic controls. The removal of MCPP at Islevbro was tested with both outlet water from filter (OW), and inlet water to filter (IW).

	Fraction of bentazone in water phase ( $^{14}\text{C}/^{14}\text{C}_0$ )				$^{14}\text{CO}_2$ -production from degradation ( $^{14}\text{CO}_2/^{14}\text{C}_0$ )			
	Microcosms		Abiotic control		Microcosms		Abiotic control	
	4 hours	13 days	4 hours	13 days	4 hours	6 days	4 hours	6 days
<b>Islevbro</b>								
MCPP OW	60-61%	64%	42-48%	57-61%	-	-	-	-
MCPP IW	60%	73%	51-57%	73-75%	-	-	-	-
Dichlorprop	72-74%	81%	26-33%	74-83%	-	-	-	-
<b>Sjælsø Plant I</b>								
MCPP	103%	63%	67-74%	67%	-	-	-	-
Dichlorprop	62-75%	60%	31-35%	62%	-	-	-	-
Glyphosate	8-9%	9%	7-8%	4%	-	-	-	-
4-nitrophenol	29%	56%	1-3%	22%	-	-	-	-
<b>Sjælsø Plant II</b>								
MCPP*	103%	112%	70-85%	92%	-	-	-	-
Dichlorprop	59-71%	101%	15-18%	103%	-	-	8-14%	-
Glyphosate	19-20%	17%	9-14%	8%	31-36%	-	42-43%	-
4-nitrophenol	28-33%	102%	3%	96%	4%	-	7-10%	-

\* low initial concentrations (0.033-0.036  $\mu\text{g/L}$ ) – uncertain results.

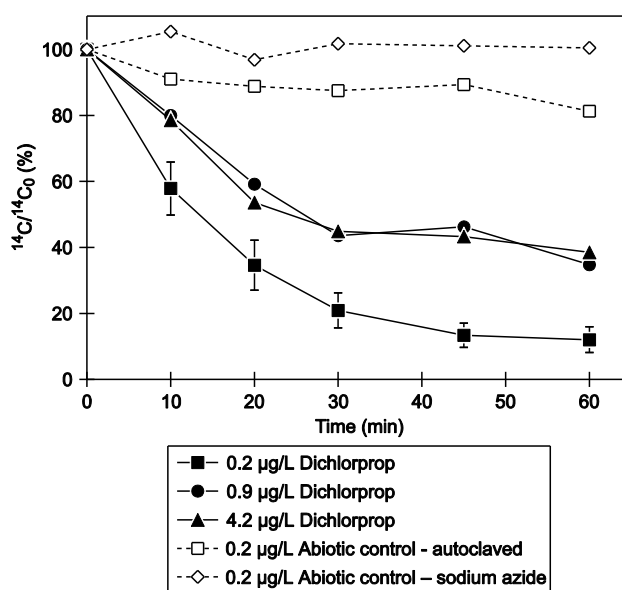
- no evident tendency in results



**Fig. 1.** Potential for degradation of dichlorprop with filter sand from three different waterworks, shown for the first six hours (A) and the entire experiments (B). Mean concentrations and standard deviation are given as a percentage of the initial concentration. Initial concentration was 0.2  $\mu\text{g/L}$  in microcosms (duplicates) and corresponding abiotic controls.

### Removal kinetics - dichlorprop

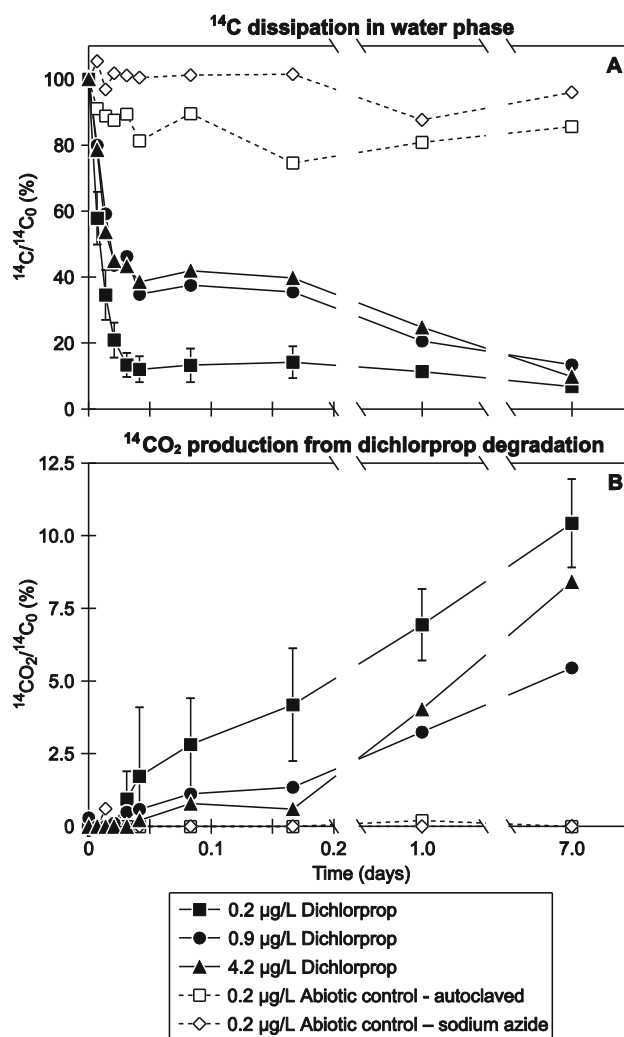
Removal of dichlorprop was investigated within the contact time of the filters on 56 minutes. Removal of dichlorprop was extremely fast during the first hour of the experiment (Figure 2), and more than 50% of the initially added dichlorprop (initial concentrations of 0.2, 0.9 and 4.2 µg/L) was removed within the first 30 minutes (Table 5). After seven days 10.4% of the removed dichlorprop had subsequently been mineralized (Figure 3).



**Fig. 2.** Removal kinetics investigated at three different initial concentrations in a short-term investigation. Microcosms contained 250 g filter sand and 100 mL water from Sjælsø waterworks Plant II. The mean concentrations and standard deviation are given as percentage of the initial concentration. Microcosms with an initial concentration of 0.2 µg/L (triplicate) are depicted along with two corresponding abiotic controls (initial concentration 0.2 µg/L, inhibited in two different ways) and two microcosms with initial concentrations of 0.9 µg/L and 4.2 µg/L.

**Table 5.** The 50% dissipation time,  $DT_{50\%}$ , for dichlorprop was read off the curves in Figure 2 at different initial concentrations.

Initial concentration (µg/L)	$DT_{50\%}$ (min)
0.2	13
0.9	26
4.2	24

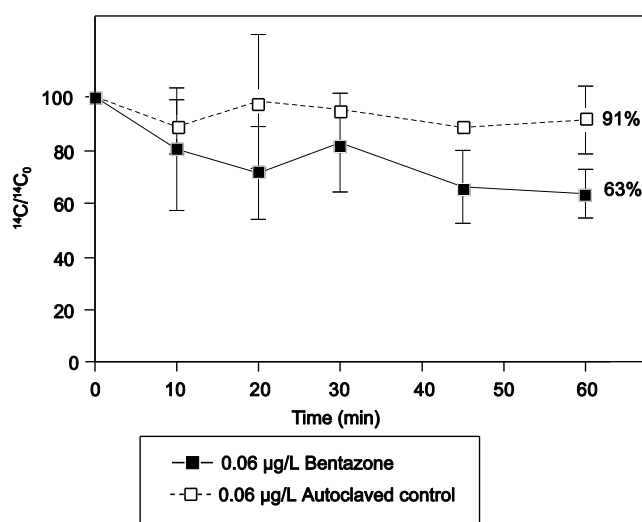


**Fig. 3.** Removal kinetics – long-term investigation. Microcosms with 250 g filter sand (Sjælsø waterworks Plant II), 100 mL water and an initial dichlorprop concentration of 0.2 µg/L (triplicates), 0.9 µg/L (one microcosm) and 4.2 µg/L (one microcosm) were investigated along with two different abiotic controls (initial concentration 0.2 µg/L). Mean values and standard deviation are shown for A) concentration of dichlorprop in the water ( $^{14}\text{C}/^{14}\text{C}_0$ ), and B)  $^{14}\text{CO}_2$  production ( $^{14}\text{CO}_2/^{14}\text{C}_0$ ) from the degradation of dichlorprop.

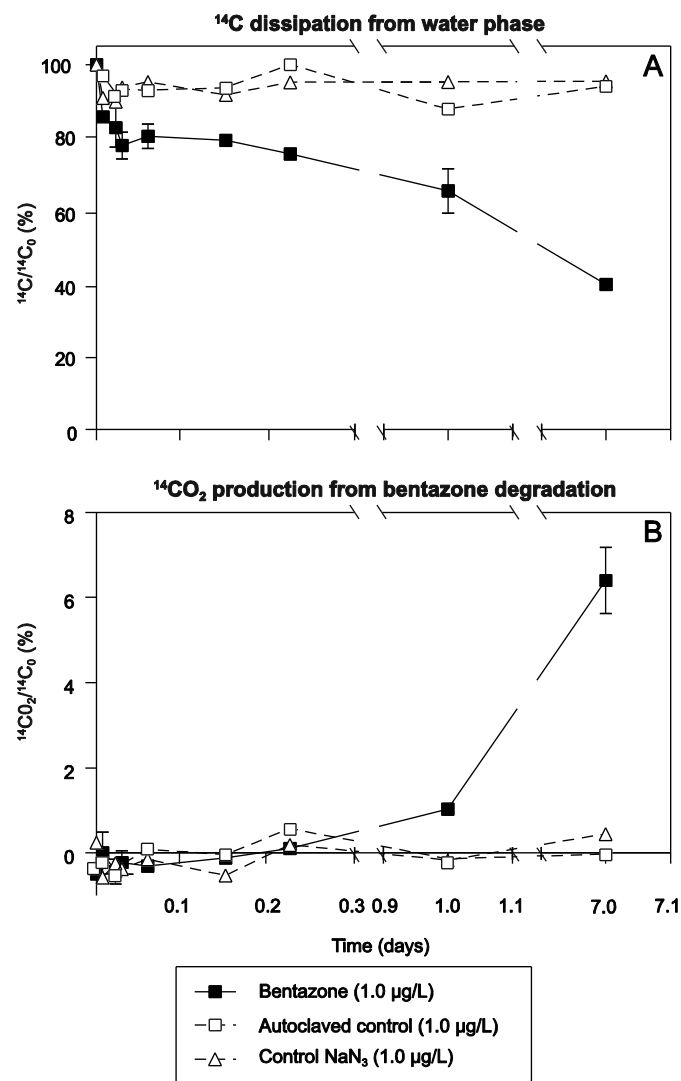


### Removal kinetics - bentazone

The removal potential and kinetics of [ $^{14}\text{C}$ -carbonyl-]bentazone was investigated with filter sand from Sjølsø plant II (Table 3). The contact time of the filter was 56 minutes and during one hour 37% [ $^{14}\text{C}$ -carbonyl-]bentazone was removed in biologically active microcosms, while only 9 % was removed in autoclaved controls (initial concentration 0.06  $\mu\text{g/L}$ ) (Figure 2X). Hence, it was possible to remove bentazone within the contact time of the rapid sand filters and the removal was primarily due to microbial activity. This was verified by another experiment, lasting for seven days (Figure 3XA). After seven days removal of bentazone led to a partial mineralization where 6.4 % of the initially added bentazone (initial concentration 1.0  $\mu\text{g/L}$ ) could be detected as  $^{14}\text{CO}_2$  in microcosms (Figure 3XB), while no mineralization could be detected in the abiotic controls.



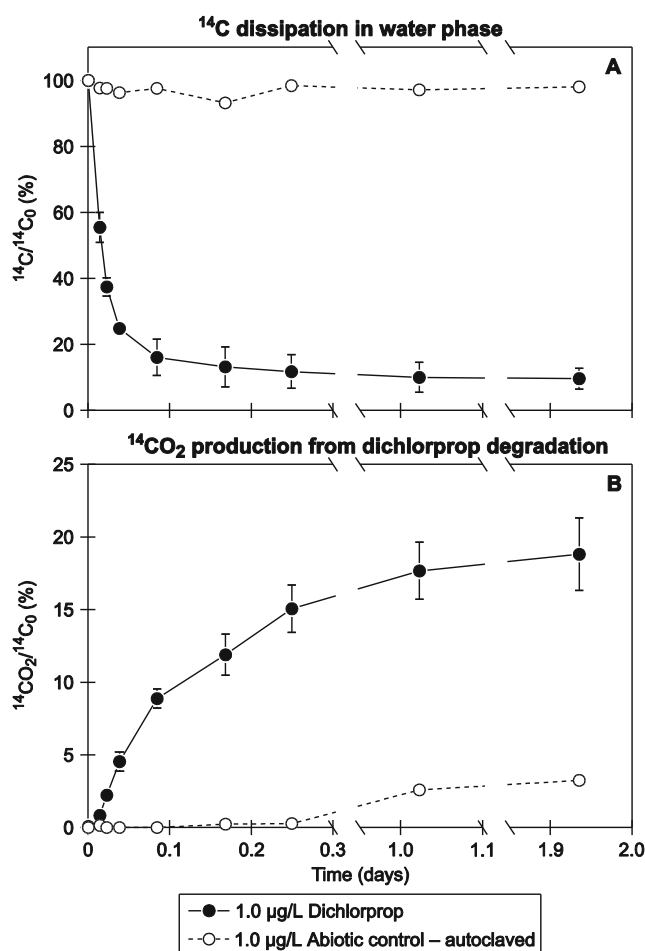
**Fig. 2X.** Removal kinetics of bentazone during one hour. Microcosms contained 250 g filter sand and 100 mL water from Sjølsø waterworks Plant II. The mean concentrations and standard deviation are given as percentage of the initial concentration. Microcosms (triplicates) are depicted along with an autoclaved control (initial concentration 0.06  $\mu\text{g/L}$ ).



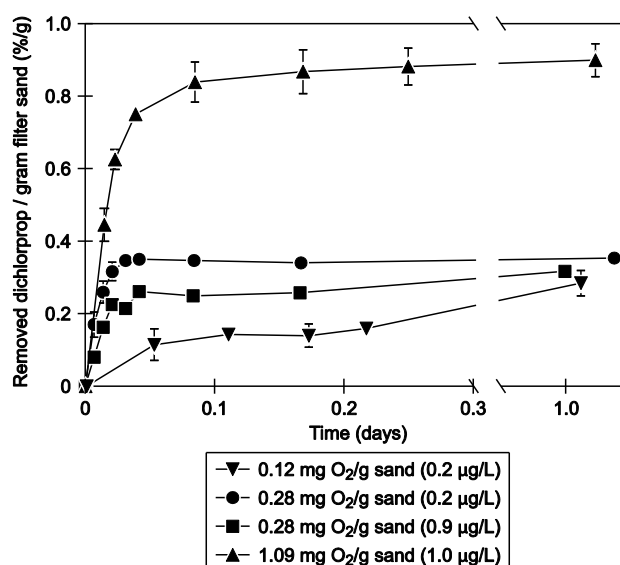
**Fig. 3X.** Removal potential of bentazone over seven days. Microcosms with 100 g filter sand (Sjælsø waterworks Plant II), 100 mL water and bentazone (triplicates) were investigated along with two different abiotic controls (initial concentration 1.0  $\mu\text{g/L}$ ). Mean values and standard deviation are shown for A) concentration of bentazone in the water ( $^{14}\text{C}/^{14}\text{C}_0$ ), and B)  $^{14}\text{CO}_2$  production ( $^{14}\text{CO}_2/^{14}\text{C}_0$ ) from the degradation of bentazone.

## Effect of oxygen

It was investigated whether differences in the removal of dichlorprop between experiments could be explained by the limited availability of oxygen. In full-scale rapid sand filters at waterworks, oxygen is easily available to microorganisms and so the experiment ‘*Effect of oxygen*’ was set up to validate the effect of oxygen on dichlorprop removal (Figure 4). After one hour, dichlorprop removal (initial concentration 0.9-1.0 µg/L) increased from 0.21 %/g filter sand to 0.75 %/g filter sand when oxygen availability increased from 0.28 mg O<sub>2</sub>/g filter sand to 1.09 mg O<sub>2</sub>/g filter sand (Figure 5). This increased the removal efficiency of the filter sand at a significance level of 99.95%.



**Fig. 4.** Removal of dichlorprop under high oxygen concentrations. Microcosms with 100 g filter sand (Sjælsø waterworks Plant II), 100 mL water and dichlorprop (triplicates) were investigated along with the one corresponding abiotic control (initial dichlorprop concentration 1.0 µg/L). Mean values and standard deviation are shown for A) concentration of dichlorprop in the water ( $^{14}\text{C}/^{14}\text{C}_0$ ), and B)  $^{14}\text{CO}_2$  production ( $^{14}\text{CO}_2/^{14}\text{C}_0$ ) from the degradation of dichlorprop.



**Fig. 5** Effect of oxygen on the removal of dichlorprop from the water phase. The available amount of oxygen per gram of filter sand was calculated in each experiment as the sum of oxygen in the water and the headspace at the start and the total added amount during the experiment. The amount of dichlorprop removed from the water phase ( $^{14}\text{C}/^{14}\text{C}_0$  (%)) per gram of filter sand in the microcosms is shown for each of the experiments. The initial concentration of dichlorprop is given in brackets.

### Complete degradation – investigations of ring-bentazone

The purpose of investigating removal with ring-bentazone was to map the impact of the position of the  $^{14}\text{C}$ -label on the measured bentazone removal. Unfortunately, the discussed difference in the removal was a result of the mix-up, so removal of ring-bentazone was compared to removal of dichlorprop.

However, the investigations with ring-bentazone confirm that bentazone was removed in contact with filter sand (Figure 6) at the time Hedegaard and Albrechtsen (2014) was published.

### Perspectives

A fraction (10%) of dichlorprop remained in the water phase regardless of the initial concentration. The lack of degradation of the residual part of dichlorprop, indicated formation of a more persistent metabolite.

## Conclusion

The investigations showed:

- A clear removal potential of the pesticides MCPP, dichlorprop, glyphosate, and *p*-nitrophenol with filter sand from rapid sand filters at Danish waterworks. The largest microbial removal was observed with filter material taken from Sjælsø Plant II.
- In filter sand from Sjælsø waterworks Plant II dichlorprop concentration in the water phase decreased as a result of microbial removal to less than 50% of the initial concentration within 30 minutes for all the tested start concentrations (0.2–4.2 µg/L). In this filter sand bentazone was also removed rapidly and decreased by 37% within one hour (initial concentration 0.06 µg/L).
- Oxygen concentration was of substantial importance for removal kinetics and removal potential of dichlorprop. Hence, the efficiency of dichlorprop removal by filter sand increased when oxygen availability increased.

Overall, this study showed that substantial pesticide removal is possible within the contact time of rapid sand filters at groundwater based waterworks, and that rapid removal is followed by a slower mineralisation of the compound. Hence, there is a potential for microbial removal of pesticides from contaminated groundwater in Danish waterworks. This is of commercial interest due to substantial attention given to the maintenance of today's water treatments.

## References

Tomlin, C. D. S., 2003. [The e-pesticide manual], version 3.0, 13<sup>th</sup> edition, British Crop Production Council (BCPC)